

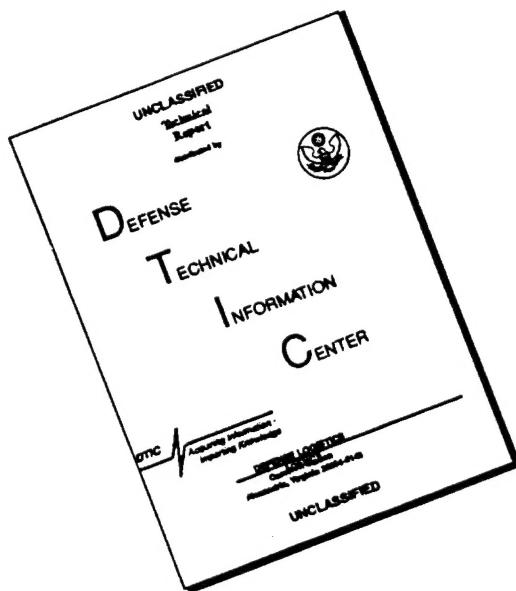
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13. ABSTRACT (Maximum 200 words)  During this project more than one-hundred block copolymers, spanning seven different chemical combinations and numerous molecular weights and compositions, were synthesized using anionic polymerization and chemical modification techniques. Phase behavior was characterized with small-angle neutron scattering (SANS) and transmission electron microscopy, guided by dynamic mechanical spectroscopy measurements. A comprehensive picture of the phase behavior of diblock copolymers near the order-disorder transition has been established. Three new morphologies, bicontinuous with Ia $\bar{3}$ d space group symmetry, hexagonally perforated layers (HPL) and hexagonally modulated layers (HML) have been identified along with the classical lamellar, cylindrical and spherical structures. Application of a new <i>in-situ</i> shear-SANS experiment has aided in elucidating the susceptibility of these phases to deformation and flow. Reciprocating shear has been shown to produce macroscopic orientation, and to shift the phase boundaries. Similar static and dynamic phenomena were found for binary mixtures of diblock copolymers, thereby demonstrating a versatile method for controlling structure and properties without the need to produce new materials at each desired composition.			
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# **Thermodynamics and Processing of Block Copolymers with NLO Application**

**Grant No.:** AF/F49620-93-1-0182

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University of Minnesota  
Minneapolis, MN 55455

## **Final Technical Report**

### **I. Introduction**

Block copolymers have fascinated scientists and engineers for more than three decades. As items of commerce this class of polymers contributes several billions of dollars annually to the U.S. economy, in products such as adhesives, polymer blends, foams, tires, and numerous other materials. However, all these applications are relatively primitive considering the remarkable microstructures and physical properties that can be obtained with block copolymers. Research over the last few years has provided a deep understanding of the molecular factors responsible for microphase separation and ordering in block copolymer melts driven in large part by advances in experimentation. Some of the most recent discoveries have been made under this AFOSR grant as described in the following sections.

### **II. Research Results**

Research under contract AF/F49620-93-1-0182 focused on four issues: i) synthesis of a variety of well-defined diblock copolymers, ii) characterization of the phase behavior of these block copolymers and block copolymer mixtures, iii) evaluation of the processibility of the resulting microstructures, and iv) growth of NLO active organic nanocrystals within ordered and oriented microdomains.

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When this work began, diblock copolymer phase behavior was predicted, and generally accepted,<sup>(1,2)</sup> to be universally described by two parameters:  $\chi N$  and  $f$ , where  $\chi$  and  $N$  are the segment-segment interaction parameter and degree of polymerization, respectively, and  $f$  is the composition (volume fraction of one block). Three decades of experimentation had placed four microstructures within the ordered region of phase space: spheres (S) packed on a BCC lattice, hexagonally packed cylinders (HEX), the ordered bicontinuous double diamond (OBDD) structure, and lamellae (LAM). The identification of the OBDD<sup>(3,4)</sup> between the HEX and LAM states in the mid 1980's was particularly noteworthy as this morphology offered a variety of potential applications ranging from selective membranes to mechanically superior nanocomposites. During the past three years the perception of block copolymer phase behavior has changed dramatically due in large part to the work performed under this contract. The notion of a universal phase diagram has been challenged by the discovery of a systematic molecular weight dependence that suggests that fluctuations play a significant role in the occurrence of complex ordered states. Three new microstructures have been identified<sup>(5-8)</sup>: hexagonally modulated lamellae (HML), hexagonally perforated lamellar (HPL), and a bicontinuous cubic morphology with  $Ia\bar{3}d$  space group symmetry (see Figure 1). (We have not found the OBDD phase in any of our samples,

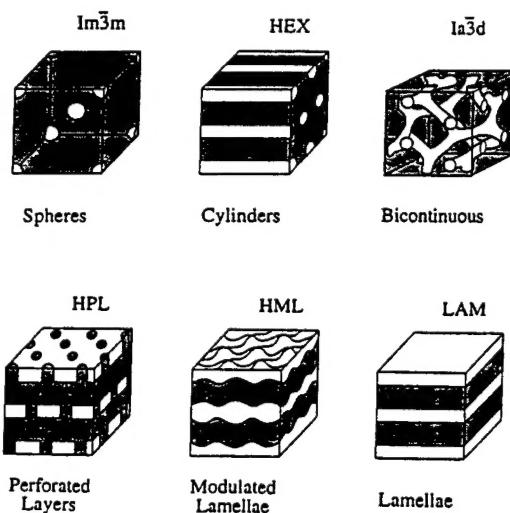


Figure 1. Block copolymer microstructures identified in diblock copolymers and blends (see Table 1). The bicontinuous, perforated layers and modulated layers are newly discovered (from ref. 5).

leading us to conclude that this morphology was originally incorrectly assigned; independent experiments by Hajduk et al.(9,10) support this conclusion.)

An in-depth examination of diblock mixtures has complemented our work with pure diblocks. Blending offers the advantage of continuous compositional control, which is crucial in quantifying the location of each ordered phase. Phase identification has been facilitated by making use of dynamic shearing devices that allow the orientation of certain microstructures prior to, and during, small angle scattering experiments. This technique has led to the discovery of epitaxial relationships between certain ordered states,(11) and in conjunction with dynamic mechanical spectroscopy (DMS) measurements, has provided a wealth of information regarding the (anisotropic) viscoelastic properties associated with each morphology.(12)

The final focus involved growth of organic NLO crystals within the ordered microdomains. This phase of the work required the development of new diblocks with a greater disparity in block polarity than we originally envisioned. This was accomplished, and we demonstrated that dye molecules could be partitioned between polar and non-polar regions of the materials.

This work has led to fourteen publications (in print, in press, or submitted) with several more currently in preparation. Our findings have forced us to pursue unanticipated questions that necessitated the development of new materials. This in turn has led to fresh insights and lines of inquiry in the area of nanostructured materials.

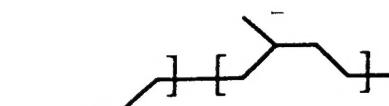
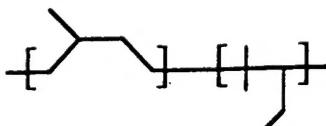
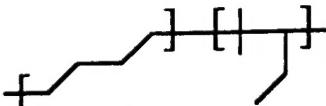
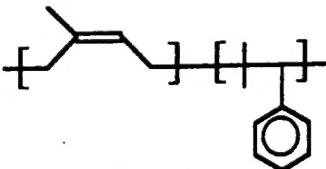
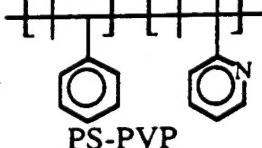
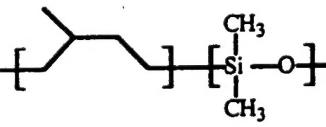
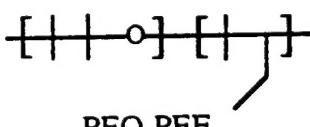
**II.a. Synthesis** All of the materials investigated in this program have been prepared in the PI's laboratories at the University of Minnesota. In order to maintain complete control over molecular weight, molecular architecture, and composition we have employed anionic polymerization augmented by catalytic hydrogenation. A description of our polymerization techniques has recently been published.(13) Characterization of the products has been accomplished using size exclusion chromatography, light scattering, and NMR. In general, 20 to 100 grams of polymer ( $1.03 \leq M_w/M_n \leq 1.15$ ) are produced per preparation, providing adequate material for a complete battery of structural and property measurements in pure and blended forms. Table 1 identifies the seven systems studied, listed from top to bottom with increasing  $\chi$ . The

most compatible materials (PE-PEP) can order (microphase separate) at 150°C when the molecular weight exceeds  $1.1 \times 10^5$  g/mole while the least compatible system (PEO-PEE) requires a molecular weight of just  $3.5 \times 10^3$  g/mole to produce an ordered phase at this temperature (see below). In total, more than 100 different polymers have been produced covering a wide range of compositions ( $0.15 < f < 0.85$ ), molecular weights, and molecular architectures. Generally, the polymers were designed to have experimentally accessible order-disorder transition (ODT) temperatures.

With the exception of the last two compounds listed in Table 1, the synthetic procedures have involved established methods.<sup>(14,15)</sup> Preparation of PEP-PDMS and PEO-PEE required innovative modifications of existing techniques. Generation of a cis 1, 4-polyisoprene block, which is the PEP precursor, necessitates the use of a lithium counterion and a non-polar hydrocarbon solvent, conditions that are not conducive to the polymerization of hexamethylcyclotrisiloxane (D3). In a collaboration with Dr. Kristoffer Almdal (Risø National Laboratory) the reactivity of this system was investigated and improved dramatically by adding controlled amounts of hexamethylphosphoramide (HMPA). Based on the results of a detailed kinetic study we were able to identify optimal reaction times that avoid the side reactions known to plague the anionic polymerization of D3 monomer. Subsequently, a heterogeneous catalytic hydrogenation scheme was developed that leads to > 99% saturation efficiency without chain degradation. The resulting overall PEP-PDMS polydispersities are typically less than 1.1.

Different approaches are required when preparing PEO-PEE, our newest class of block copolymers. These methods play a central role in the proposed research program as described in the following section. The PEO-PEE polymerization is carried out in two stages. First, anionically grown polybutadiene (90% 1,2 addition) is terminated with ethylene oxide to yield hydroxyterminated polybutadiene. Subsequent catalytic hydrogenation yields the corresponding PEE. This aliphatic polyol is then treated with sodium naphthalene to give the alkoxide which serves as a macroinitiator for ethylene oxide. Each step of this process is highly efficient leading to

Table 1  
Model Diblock Copolymer Systems

Species	# samples prepared	$10^3 M_{ODT}$ ( $T=150^\circ C$ )	<sup>†</sup> Phases Identified
 PE-PEP	14	110	L, C, S, HML, HPL
 PEP-PEE	25	60	L, C, S, HML, MPL, Ia3d
 PE-PEE	23	30	L, C, S, HML, HPL, Ia3d
 PI-PS	19	18	L, C, S, HPL, Ia3d
 PS-PVP	20	18	L, C, HPL, Ia3d
 PEP-PDMS	4	8	L, Ia3d
 PEO-PEE	8	4	L, C, Ia3d

<sup>†</sup> L = lamellae; C = cylinders; S = sphere; HML = hexagonally modulated lamellae; HPL = hexagonally perforated layers; Ia3d = bicontinuous

overall yields of 98% or more and tight control over the product composition and molecular weight.

**II.b. Phase Behavior** As part of this research program we have developed robust procedures which allow us to identify how composition, molecular weight, and temperature influence block copolymer phase behavior. Our protocol relies on three characterization methods: dynamic mechanical spectroscopy (DMS), small-angle scattering (SANS and SAXS), and transmission electron microscopy (TEM). DMS is a versatile technique that provides a sensitive "fingerprint" of the linear viscoelastic properties as a function of frequency and temperature. Phase transitions between ordered (or disordered) states are accompanied by changes in the dynamic elastic and loss moduli ( $G'$  and  $G''$ ); a brief discussion of the mechanical spectra associated with each morphology is presented in section IIId. DMS measurements (e.g.,  $G'(T)$  at a fixed frequency) provide the most efficient method for establishing phase transition temperatures. We have used the Rheometrics RMS800 and RSAII spectrometers for this purpose.

Ordered state symmetry and the quantitative determination of microdomain spacing are best addressed by small-angle scattering experiments. SANS offers the advantages of selective deuterium labeling and easy implementation of dynamic shearing devices (see Section IIc), while SAXS is a higher resolution technique. We have made use of both methods in this work. SANS experiments were conducted at NIST (NIST/Exxon/U.Mn 30 meter instrument) and at the Risø (Danish) National Laboratory (12 meter instrument). X-ray scattering has been done in collaboration with Prof. A.J. Ryan on the synchrotron source at Daresbury, England, and using a rotating anode-based instrument with Prof. Sol Gruner of Princeton University.

TEM provides graphic real-space images of polymer microstructure. However, as the misassignment of the OBDD morphology<sup>(3,4,10)</sup> demonstrates, sole reliance on this method can be dangerous. Moreover, TEM measurements require staining and microtoming which cannot be conducted at arbitrary temperatures. Nevertheless, this technique is an ideal complement to SANS, SAXS and DMS.

An illustration of the combined use of these techniques is given in Figure 2 for a PI-PS specimen<sup>(7,8)</sup>. The  $G'(T)$  trace (not shown) revealed sharp increases and decreases in elasticity at specific temperatures associated with order-order and order-disorder transitions (OOT and ODT). A synchrotron X-ray scattering measurement (Fig. 2a), conducted at a temperature corresponding to the highest  $G'$  regime, produced a complement of reflections consistent with the  $Ia\bar{3}d$  cubic space group; the arrows indicate the expected peak positions for this assignment. Finally, a TEM image taken from a specimen annealed at the same temperature (Figure 2b) confirms that the morphology is bicontinuous. Each of these experiments contributed an important element to our identification of this phase as bicontinuous  $Ia\bar{3}d$ . Note that the SAXS data conclusively rule out the OBDD phase, which might have been associated with the TEM image.<sup>(3,4)</sup>

**Pure Diblocks** Using these methods we have established the phase behavior for five of the systems listed in Table 1. These can be grouped into three categories: i) PE-PEP, ii) PEP-PEE and PE-PEE and iii) PI-PS and PS-PVP. The associated phase diagrams, plotted in terms of the reduced parameter  $N$  and  $f$ , are given in Figure 3. Classifying these phase diagrams represents a major accomplishment of this project. Two general conclusions can be drawn from this figure. First, block copolymer phase behavior is not universal in  $\chi N$  and  $f$  as previously assumed; a

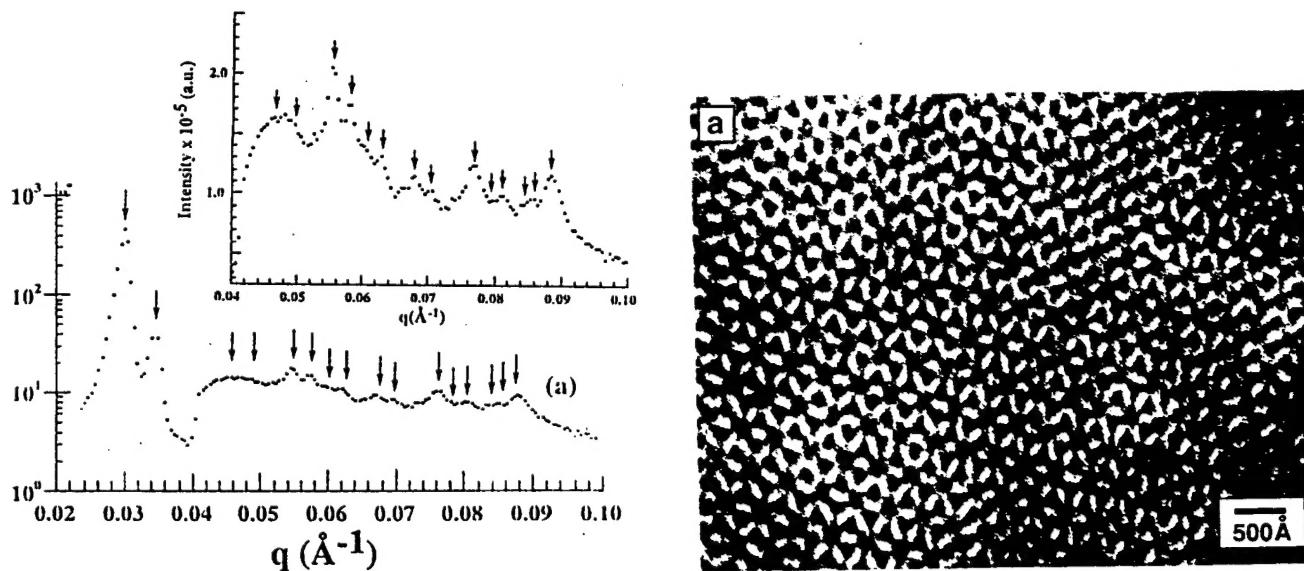


Figure 2. SAXS pattern (left) and TEM micrograph (right) obtained from a PI-PS diblock copolymer that has bicontinuous morphology. Arrows indicate anticipated reflections for the  $Ia\bar{3}d$  space group symmetry. This data rules out the OBDD phase (from ref. 7).

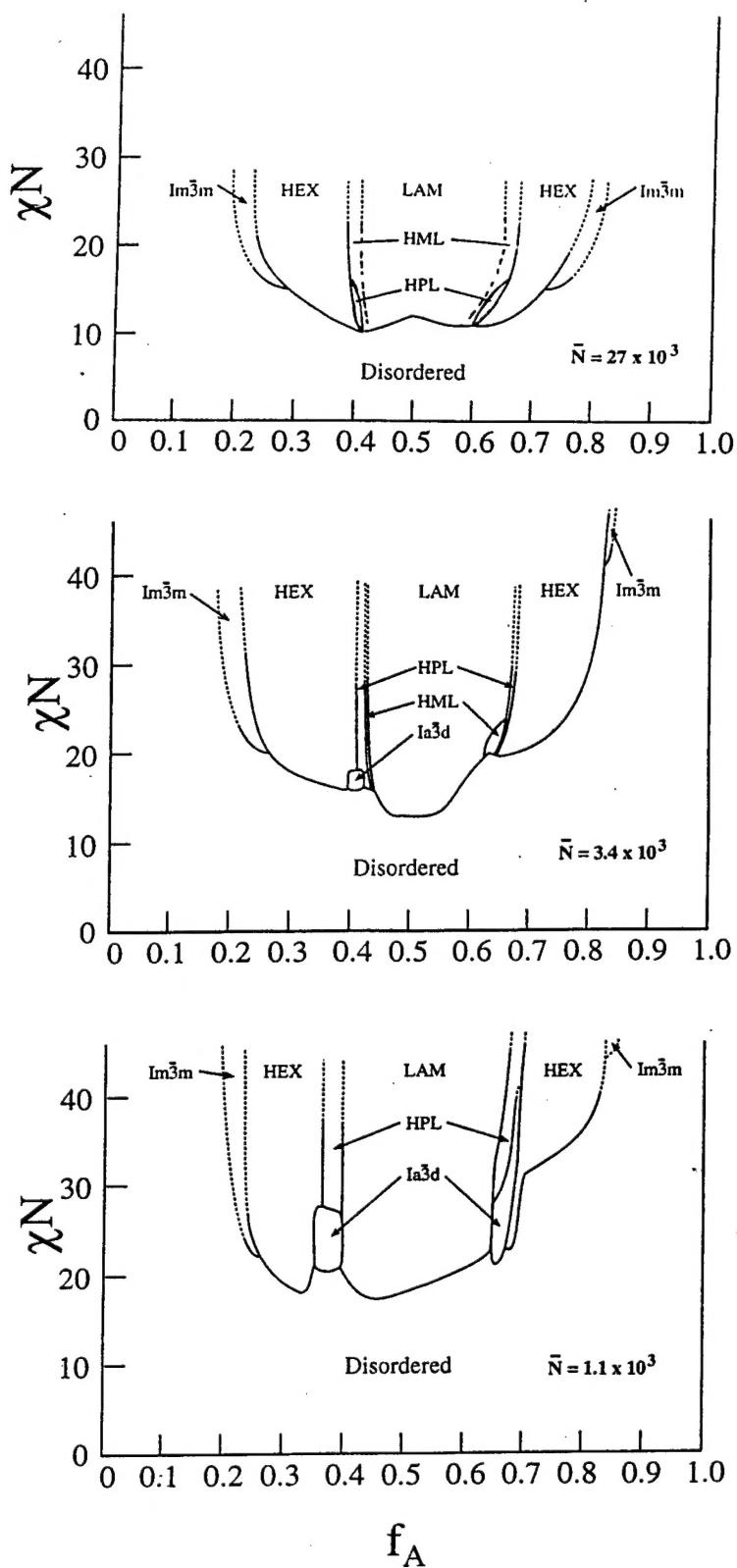


Figure 3. Phase behavior for three classes of diblock copolymer:  $\bar{N} = 27 \times 10^3$  (PE-PEP),  $\bar{N} = 3.4 \times 10^3$  (PE-PEE and PE-PEE), and  $\bar{N} = 1.1 \times 10^3$  (PI-PS and PS-PVP). These results, obtained by studying more than 100 diblock copolymers (see Table 1) demonstrate that diblock copolymer phase behavior is not universal in  $\chi N$  and  $f$ . Reducing molecular weight (i.e.,  $\bar{N}$ ) stabilizes the bicontinuous Ia $\bar{3}$ d phase (from ref. 5).

distinct pattern of structures evolve as the overall molecular weight is reduced. Apparently, the bicontinuous Ia $\bar{3}$ d phase is *stabilized* by reducing the overall molecular size, as it is completely absent from the highest molecular weight system (PE-PEP). Second, the phase diagram is asymmetrically distributed around  $f = 1/2$ . This feature can be attributed to con-formational asymmetry,<sup>(5,16)</sup> a property related to differences in the coil-dimensions of each block, over and above what is accounted for by  $f$ .

Our most recent analyses of the lowest molecular weight systems (PEO-PEE and PEP-PDMS) have confirmed the bicontinuous Ia $\bar{3}$ d phase in both, and indicate that the window in  $\chi N$  where this phase occurs may be expanded.<sup>(17)</sup>

**Diblock Blends** Exploiting the remarkable properties associated with each of the microstructures illustrated in Figure 1 requires rather precise control of  $\chi N$  and  $f$  (see Figure 3). The most efficient method for doing this is to blend two or more diblocks having different compositions and/or molecular weights. However, introducing additional components leads to additional thermodynamic degrees of freedom that could compromise creation of the desired microstructure. We have investigated this issue using the PE-PEE<sup>(12)</sup> and PS-PVP<sup>(18)</sup> systems. These represent two extremes in conformational asymmetry:  $\epsilon_{\text{PE-PEE}} \approx 3$  and  $\epsilon_{\text{PS-PVP}} \approx 1.3$ . (Here  $\epsilon = \beta_1^2/\beta_2^2$  with  $\beta^2 = b^2/6v_0$  in which  $b$  and  $v_0$  are the statistical segment length and volume, respectively; a detailed discussion of the concept of conformational asymmetry is provided in references 5 and 6). In both cases we discovered that the pure diblock phase behavior near the order-disorder transition was nearly duplicated by the binary blends. A representative PE-PEE phase diagram,<sup>(12)</sup> obtained by blending  $f_{\text{PE}} = 0.37$  and  $f_{\text{PE}} = 0.46$  materials is shown in Figure 4a. The bicontinuous Ia $\bar{3}$ d phase occurs between the cylindrical and lamellar states at  $0.39 < f_{\text{PE}} < 0.42$  within roughly 100 degrees (or less) of the ODT temperature. At lower temperatures (higher  $\chi N$ ) the HPL phase, and possibly a biphasic window, occur. A surprising finding was that the composition range of the bicontinuous window could be shifted significantly

by mixing different materials. As shown in Figure 4b the complex phases are found at  $0.31 < f_{PE} < 0.34$  when  $f_{PE} = 0.25$  and  $f_{PE} = 0.49$  diblocks are blended. Overall, our blending results confirm that the general phase behavior seen with pure diblocks can be duplicated in blends.

**II.c. Processing** Most polymer applications rely on deformation and flow to produce a final product. Block copolymer melts respond in a variety of ways to such processing steps, offering unique opportunities for creating anisotropic nanostructures. We have combined our rheological and SANS capabilities in examining this issue using the well characterized materials described earlier in this section. During the course of this research an *in-situ* dynamic shearing device was developed that could be operated while conducting SANS measurements. Using this technique we have explored how shear-rate and strain amplitude influence microdomain order and orientation for several of the morphologies found in Figure 1.

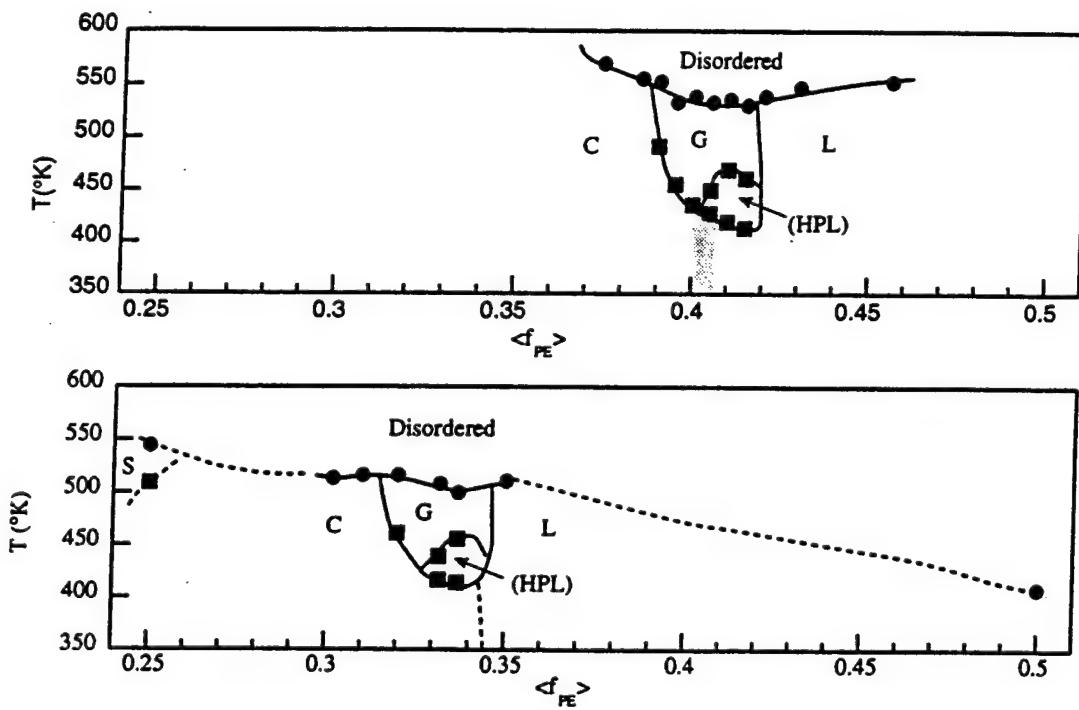


Figure 4. Phase behavior of two sets of PE-PEE binary diblock copolymer blends. The top figure resulted from a mixture of  $f_{PE} = 0.37$  and  $0.46$  while the bottom figure represents the phase diagram of  $f_{PE} = 0.25$  and  $0.50$  mixtures. These results show that blending can be used to produce the same microstructures found in pure diblocks. C, G, and L refer to cylinders, Ia $\bar{3}$ d bicontinuous and lamellae (to be published).

Near the ODT application of shear stabilizes the lamellar<sup>(19)</sup> and cylindrical<sup>(20)</sup> phases as illustrated in Figure 5 for an asymmetric PEP-PEE diblock copolymer melt. At a sufficiently high shear rate the disordered (fluctuating) state transforms into highly aligned hexagonally packed cylinders, with the (10) plane lying parallel to the shear plane. This transformation is clearly evidenced by the development of well-resolved Bragg reflections along the  $q_z$  scattering wavevector and the concomitant loss of the concentric ring of scattering that characterizes the disordered state. Cessation of shearing leads to complete recovery of the initial isotropic material. If the sheared material is cooled, or simply processed below the ODT, a permanent state of alignment is achieved.<sup>(21)</sup>

We have conducted this type of experiment on a variety of the materials listed in Table 1 while in the lamellar, cylindrical, spherical, and perforated lamellar morphologies. With the exception of spheres, shear always induces alignment although the detailed orientation depends on shear rate and temperature (relative to T<sub>ODT</sub>) in a complicated manner. BCC packed spheres behave quite differently.<sup>(22)</sup> Dynamic shearing may induce order (low shear rates) or disorder (higher shear rates), or may induce an order-order phase transition.

Production of well aligned low symmetry morphologies yielded an unanticipated discovery<sup>(11)</sup>: Growth of the bicontinuous Ia $\bar{3}$ d microstructure from hexagonally packed cylinders (HEX) and hexagonally perforated layers (HPL) is mediated by epitaxial relationships, analogous to those encountered in low molecular weight crystals. An example of this effect is shown in Figure 6 where a shear aligned PS-PVP blend specimen (HEX phase) is heated into the bicontinuous Ia $\bar{3}$ d phase. SANS patterns, obtained with two neutron beam orientations, reveals that the six-fold hexagonal direction transforms into the three-fold cubic axis. The associated real-space epitaxial relationship is also depicted. Identification of the bicontinuous phase was facilitated by the azimuthal angular relationships between principal scattering peaks made possible by this fascinating epitaxy.

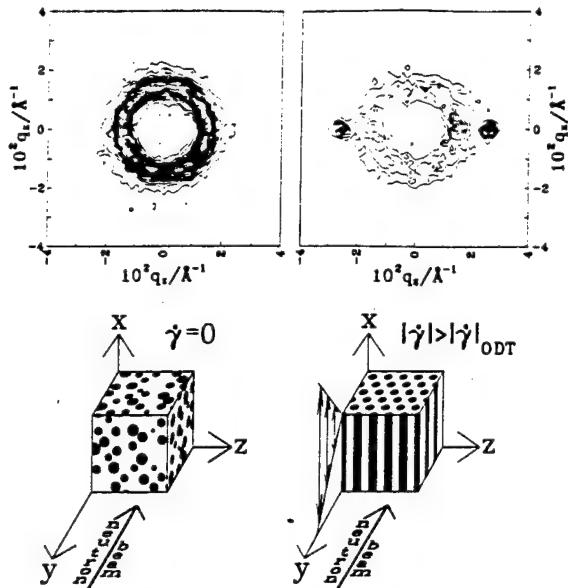


Figure 5. Influence of shear on a block copolymer melt (PEP-PEE,  $f_{\text{PEP}} = 0.77$ ) near the order-disorder transition. Dynamic shear is shown to order this material several degrees above  $T_{\text{ODT}}$ . The contour plots are SANS patterns obtained while shearing with the *in-situ* device (from ref. 19).

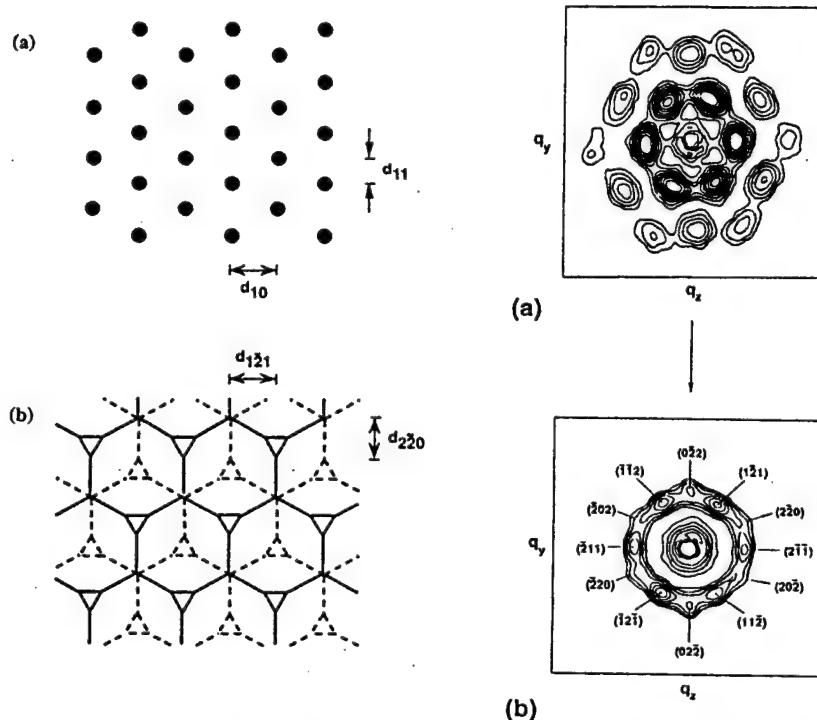


Figure 6. Epitaxial relationship established between the cylindrical (upper left) and  $Ia\bar{3}d$  bicontinuous (lower left) phases. The SANS patterns (right side) were obtained with the neutron beam coincident with the initial shear aligned cylinder axis (from ref. 11).

**II.d. Mechanical Properties** Access to the microstructures illustrated in Figure 1 has permitted us to start characterizing the linear viscoelastic properties of these materials. Each of the six microstructures exhibits a unique viscoelastic "fingerprint." However, quantitative comparison of these can be difficult due to the wide range of relaxation times associated with the different systems. The most meaningful assessment is made by examining all the microstructures using a single class of compounds. An example is provided in Figure 7 based on the PE-PEE system.<sup>(12)</sup>

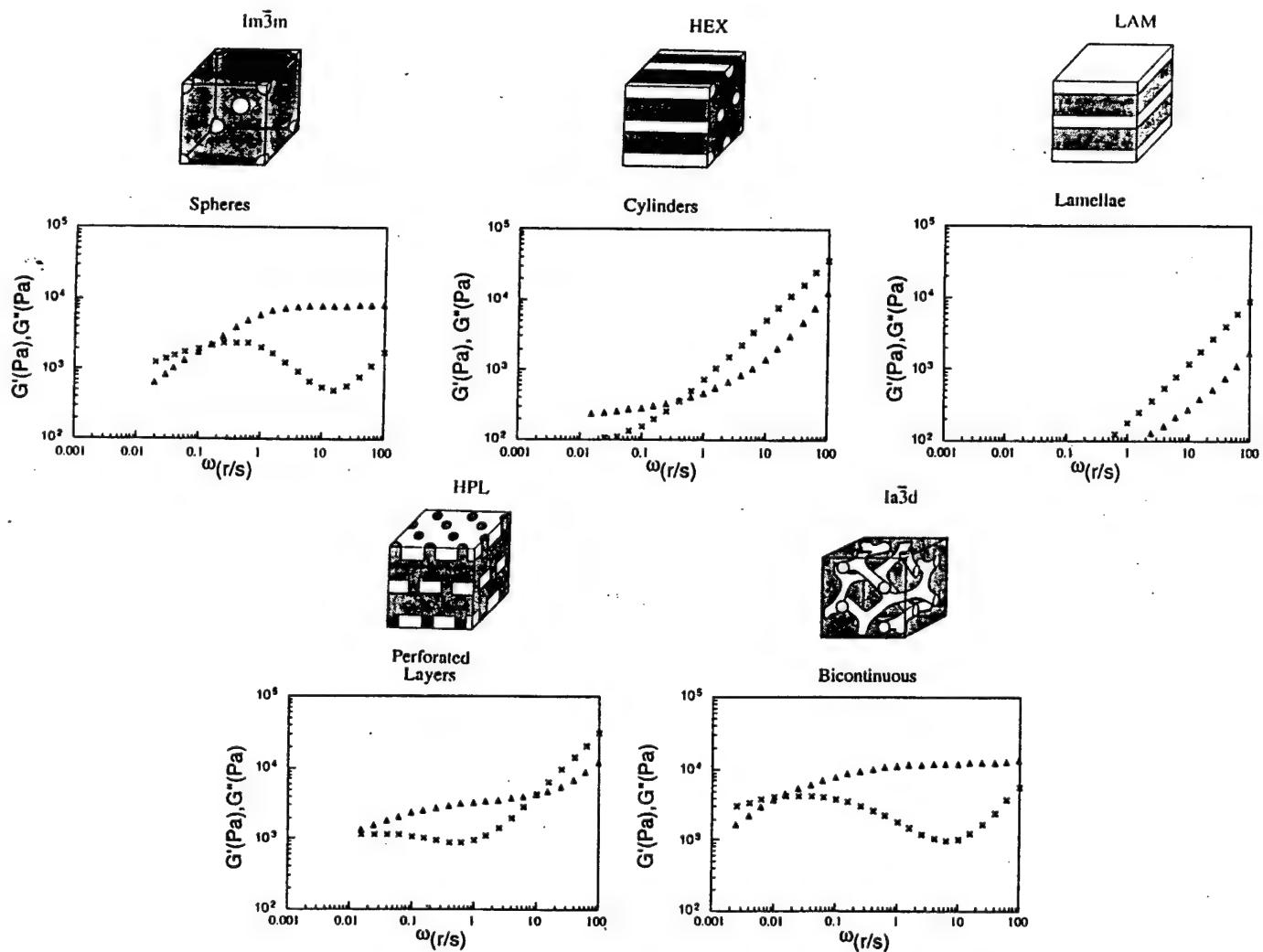


Figure 7. Dynamic mechanical spectra associated with five of the microstructures identified in PE-PEE diblock copolymers;  $\nabla$  and  $X$  represent  $G'$  and  $G''$  respectively. Variations in the microstructure produce enormous changes in the rheological properties.

The dynamic mechanical elastic and loss moduli ( $G'$  and  $G''$ ) are compared for five phase states as a function of frequency. These morphologies exhibit grossly different properties ranging from nearly fluid-like (lamellae and cylinders) to virtual solids (BCC spheres and bicontinuous  $Ia\bar{3}d$ ). In general,  $G'$  increases as the connectivity of the morphology increases, from LAM to HEX to HPL and finally bicontinuous. However, this logic cannot explain why the BCC sphere response is nearly indistinguishable from that associated with the bicontinuous material. Although we have no firm explanation for this unexpected result, it suggests that the ordering, rather than symmetry microstructure topology, plays a predominant role in determining the linear viscoelastic properties.

**II.e. NLO Application** Finally, we have been exploring ways to grow organic crystals that exhibit second-order non-linear optical susceptibility within ordered block copolymer material. If such crystals were oriented by application of an electric field during growth, the confinement provided by the microdomain walls might impart thermal stability. Our initial efforts to accomplish this long-term goal involve identifying suitable block copolymers that will selectively partition chromophores, and then permit crystallization upon cooling. This part of the program was conducted in collaboration with Prof. Mike Ward, of the Chemical Engineering and Materials Science Department at the University of Minnesota, who specializes in organic crystal growth and morphology.

We prepared block copolymers with progressively greater segment-segment interaction parameters ( $\chi$ ) in an effort to completely solubilize model NLO organic compounds within the minority microphase of a diblock copolymer. Three chromophores have been examined: *para*-nitroaniline (PNA), *meta*-nitroaniline (MNA) and 4-chloro-*para*-nitroaniline (CNA). The last of these gave the best results, and the remaining remarks will focus on this compound. A combination of infrared (IR) and wide-angle X-ray scattering measurements were used to characterize the blends. Certain IR absorbences, such as the symmetric N-H stretch, were found to be strongly influenced by the state of mixing, and these were followed as a function of temperature, composition, and annealing time.

We studied mixtures of chromophore in PI-PS, PS-PVP, and PEO-PEE. Only PEO-PEE exhibited suitable partitioning of the dyes. As much as 50% by weight of CNA could be mixed into a  $f_{PEO} = 0.33$  diblock. However, we discovered that CNA and PEO form a complex at room temperature leading to a new, broad X-ray reflection and IR absorbences that are distinctly different than either the dissolved (liquid) or crystalline states. We were encouraged by the level of loading achieved. Electric field poling experiments will be required to determine whether molecular orientation is possible with these materials.

### II.f. Publications resulting from this grant

"Synthesis and Characterization of Model Polyalkane-Poly(ethyleneoxide) Block Copolymers," M.A. Hillmyer, F.S. Bates, *Macromolecules*, submitted.

"Complex Lyotropic-Like Phase Behavior in Solvent Free Surfactants," M.A. Hillmyer, F.S. Bates, A. Ryan, P. Fairclough, K. Almdal, K. Mortensen, *Science*, **271**, 976 (1996).

"Phase Behavior of Pure Diblocks and Binary Diblock Blends of PE-PEE," J. Zhao, B. Majumdar, M.F. Schulz, F.S. Bates, K. Almdal, K. Mortensen, D.A. Hajduk, S.M. Gruner, *Macromolecules*, **29**, 1204 (1996).

"Isotropic and Anisotropic Composition Fluctuations Close to the Order-to-Disorder Transition in an Asymmetric Diblock Copolymer Melt Subjected to Reciprocating Shear Fields," K. Almdal, K. Mortensen, K.A. Koppi, M. Tirrell, F.S. Bates, *J. Phys. II (France)*, **6**, 617 (1996).

"Phase Behavior of PS-PVP Diblock Copolymers," M.F. Schulz, A.K. Khandpur, F.S. Bates, K. Almdal, K. Mortensen, D.A. Hajduk and S.M. Gruner, *Macromolecules*, **29**, 2857 (1996).

"The Polyisoprene-Polystyrene Diblock Copolymer Phase Diagram Near the Order-Disorder Transition," A.K. Khandpur, S. Förster, F.S. Bates, I.W. Hamley, A.J. Ryan, W. Bras, K. Almdal, K. Mortensen, *Macromolecules*, **28**, 8796 (1995).

"Variable Shear-Induced Orientation of a Diblock Copolymer Hexagonal Phase," T. Tepe, M.F. Schulz, J. Zhao, M. Tirrell, F.S. Bates, K. Mortensen, K. Almdal, *Macromolecules*, **28**, 3008 (1995).

"Isotactic Polypropylene-Compatible Block Copolymer," F.S. Bates, A. Kumar, M.F. Schulz, *J. Polym. Sci., Polym. Phys.*, **33**, 1423 (1995).

"Order and Disorder in Symmetric Diblock Copolymer Melts," J.H. Rosedale, F.S. Bates, K. Almdal, K. Mortensen, G.D. Wignall, *Macromolecules*, **28**, 1429 (1995).

"Complex Layered Phases in Asymmetric Diblock Copolymers," I.W. Hamley, M.D. Gehlsen, A.K. Khandpur, K.A. Koppi, J.H. Rosedale, M.F. Schulz, F.S. Bates, K. Almdal, K. Mortensen, *J. Phys. II (France)*, **4**, 2161 (1994).

"Complex Phase Behavior of PI-PS Diblock Copolymers Near the Order-Disorder Transition," S. Förster, A.K. Khandpur, J. Zhao, F.S. Bates, I. W. Hamley, A.J. Ryan, W. Bras, *Macromolecules*, **27**, 6922 (1994).

"Fluctuations, Conformational Asymmetry and Block Copolymer Phase Behavior," F.S. Bates, M.F. Schulz, A.K. Khandpur, S. Förster, J.H. Rosedale, K. Almdal, K. Mortensen, *Faraday Discuss. Chem. Soc.*, **98**, 7 (1994).

"Influence of Shear on the Hexagonal-to-Disorder Transition in a Diblock Copolymer Melt," F.S. Bates, K.A. Koppi, M. Tirrell, K. Almdal, K. Mortensen, *Macromolecules*, **27**, 5934 (1994).

"Epitaxial Hexagonal-to-Cubic Phase Transition in a Block Copolymer Melt," M.F. Schulz, F.S. Bates, K. Almdal, K. Mortensen, *Phys. Rev. Lett.*, **73**, 86 (1994).

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### **III. References**

1. F.S. Bates and G.H. Fredrickson, *Ann. Rev. Phys. Chem.* **41**, 525 (1990).
2. F.S. Bates, *Science*, **251**, 898 (1991).
3. E.L. Thomas, D.B. Alward, D.J. Kinning, D.C. Martin, D.L. Handlin and L.J. Fetters, *Macromolecules*, **19**, 2197 (1986).
4. H. Hasegawa, H.Tanaka, K. Yamasaki and T. Hashimoto, *Macromolecules*, **20**, 1651 (1987).
5. F.S. Bates, M.F. Schulz, A.K. Khandpur, S. Förster, J.H. Rosedale, K. Almdal and K. Mortensen, *Faraday Discuss.*, **98**, 000 (1994).
6. I.W. Hamley, M.D. Gehlsen, A.K. Khandpur, K.A. Koppi, J.H. Rosedale, M.F. Schulz, F.S. Bates, K. Almdal and K. Mortensen, *J. Phys. II France* **4**, 2161 (1994).
7. S. Förster, A.K. Khandpur, J. Zhao, F.S. Bates, I.W. Hamley, A.J. Ryan and W. Bras, *Macromolecules*, **27**, 6922 (1994).
8. A.K. Khandpur, S. Förster, F.S. Bates, I.W. Hamley, A.J. Ryan, W. Bras, K. Almdal and K. Mortensen, *Macromolecules*, **28**, 8796 (1995).
9. D.A. Hajduk, P.E. Harper, S.M. Gruner, C.C. Honekar, G. Kim, E.L. Thomas and L.J. Fetters, *Macromolecules* **27**, 4063 (1994).
10. D.A. Hajduk, P.E. Harper, S.M. Gruner, C.C. Honekar, E.L. Thomas and L.J. Fetters, *Macromolecules* **28**, 2570 (1995).
11. M.F. Schulz, F.S. Bates, K. Almdal and K. Mortensen, *Phys. Rev. Lett.* **73**, 86 (1994).
12. J. Zhao, B. Majumdar, M.F. Schulz, F.S. Bates, K. Almdal, K. Mortensen, D.A. Hajduk and S.M. Gruner, *Macromolecules*, **29**, 1204 (1996).
13. S. Ndoni, C.M. Papadakis, F.S. Bates and K. Almdal, *Rev. Sci. Instru.* **66**, 1090 (1995).
14. F.S. Bates, J.H. Rosedale, H.E. Bair and T.P. Russell, *Macromolecules* **22**, 2557 (1989).
15. R.N. Young, R.P. Quirk and L.J. Fetters, *Adv. Polym. Sci.* **56**, 1 (1984).

16. F.S. Bates and G.H. Fredrickson, *Macromolecules* **27**, 1065 (1994).
17. M.A. Hillmyer, F.S. Bates, A. Ryan, P. Fairclough, K. Almdal, K. Mortensen, *Science*, **271**, 976 (1996).
18. M.F. Schulz, A.K. Khandpur, F.S. Bates, K. Almdal, K. Mortensen, D.A. Hajduk and S.M. Gruner, *Macromolecules*, **29**, 1091 (1996).
19. K. A. Koppi, M. Tirrell, F.S. Bates, *Phys. Rev. Lett.* **70**, 1449 (1993).
20. F.S. Bates, K.A. Koppi, M. Tirrell, K. Almdal and K. Mortensen, *Macromolecules* **27**, 5934 (1994).
21. K. Almdal, K.A. Koppi, F.S. Bates and K. Mortensen, *Macromolecules* **25**, 1743 (1992).
22. K.A. Koppi, M. Tirrell, F.S. Bates, K. Almdal and K. Mortensen, *J. Rheol.* **38**, 999 (1994).